(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 587 550 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
09.12.1998 Bulletin 1998/50

(51) Int Cl.[6]: **C11D 3/00**, C11D 3/37

(21) Application number: **93870106.7**

(22) Date of filing: **09.06.1993**

(54) Surfactant containing dye transfer inhibiting compositions

Tenside enthaltende Zusammensetzungen zur Verhinderung der Farbstoffübertragung

Compositions pour éviter le transfert de colorant contenant des agents tensio-actifs

(84) Designated Contracting States:
BE DE ES FR GB IT

(30) Priority: **15.07.1992 EP 92202168**
26.04.1993 EP 93201198
06.11.1992 EP 92870182

(43) Date of publication of application:
16.03.1994 Bulletin 1994/11

(73) Proprietor: **THE PROCTER & GAMBLE COMPANY**
Cincinnati, Ohio 45202 (US)

(72) Inventors:
- **Fredj, Abdennaceur**
  B-1120 Brussel (BE)
- **Johnston, James Pyott**
  B-3090 Overijse (BE)
- **Thoen, Christiaan Arthur Jacques Kamiel**
  B-9120 Haasdonk (BE)

(74) Representative: **Canonici, Jean-Jacques et al**
Procter & Gamble European Technical Center N.V.
Temselaan 100
1853 Strombeek-Bever (BE)

(56) References cited:
EP-A- 135 217
EP-A- 265 257
EP-A- 327 927
EP-A- 508 358

EP 0 587 550 B1

Description

Field of the Invention

The present invention relates to a composition and a process for inhibiting dye transfer between fabrics during washing. More in particular, this invention relates to dye transfer inhibiting compositions comprising polyamine N-oxide containing polymers and surfactants.

Background of the Invention

Detergent compositions useful for cleaning purposes, such as laundering of fabrics, have commonly utilized a variety of surfactants.

The ability of detergent compositions to clean a large variety of soils and stains from other fabrics present in the typical load of laundry is of high importance in the evaluation of detergent performance. Each surfactant has both strenghts and weaknesses.

Consequently, detergent compositions are formulated with more than one surfactant active in order to maximize advantages and minimize disadvantages.

The relative ability of each surfactant to meet various performance criteria is among others depending on the presence of adjunct detergent ingredients.

One of the types of adjunct detergent ingredients that is added to detergent compositions are dye transfer inhibiting polymers.

Said polymers are added to detergent compositions in order to inhibit the transfer of dyes from colored fabrics onto other fabrics washed therewith. These polymers have the ability to complex or adsorb the fugitive dyes washed out of dyed fabrics before the dyes have the opportunity to become attached to other articles in the wash.

Polymers have been used within detergent compositions to inhibit dye transfer.

EP-A-135 217 discloses water-soluble ethoxylated amine oxides selected from ethoxylated monoamine oxides, ethoxylated diamine oxides, ethoxylated polyamine oxides and/or ethoxylated amine oxide polymers, having clay soil removal/antiredeposition properties useful in detergent compositions.

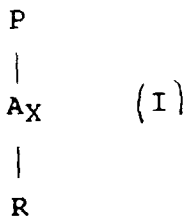
It has now been found that polyamine N-oxide containing polymers are very compatible with surfactant systems. In addition, it has been found that the dye transfer inhibiting performance has been increased in the presence of certain surfactants.

This finding allows us to formulate detergent compositions which have both excellent dye transfer inhibiting properties and overall detergency performance.

According to another embodiment of this invention a process is also provided for laundering operations involving colored fabrics.

Summary of the Invention

The present invention relates to inhibiting dye transfer compositions comprising a polymer selected from polyamine N-oxide containing polymers which contain units having the following structure formula (I) :

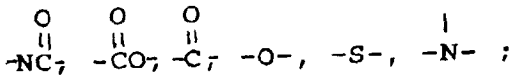


(I)

wherein

P is a polymerisable unit, whereto the N-O group can be attached to or wherein the N-O group forms part of the polymerisable unit or a combination of both.

A is

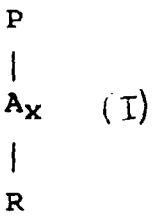


x is 0 or 1;

R are aliphatic, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group form part of these groups,with the proviso that R is not an ethoxylated group,

and a surfactant system.

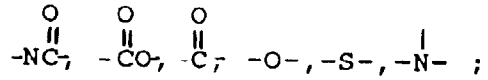
In another embodiment, the present invention relates to the use of a polymer selected from polyamine N-oxide containing polymers which contain units having the following structure formula (I) :



wherein

P is a polymerisable unit, whereto the N-O group can be attached to or wherein the N-O group forms part of the polymerisable unit or a combination of both

A is

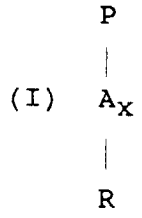


x is 0 or 1;

R are aliphatic, ethoxylated aliphatic, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups, and a surfactant system, for inhibiting dye transfer, between fabrics during washing.

Detailed description of the invention

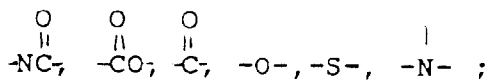
The compositions of the present invention comprise as an essential element polyamine N-oxide containing polymers which contain units having the following structure formula :



wherein

P is a polymerisable unit, whereto the R-N-O group can be attached to or wherein the R-N-O group forms part of the polymerisable unit or a combination of both.

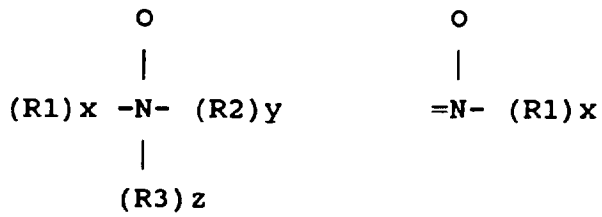
A is



x is 0 or 1;

R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures :



wherein

R1, R2, R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups.

The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups.

One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group is attached to the R-group.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit.

Preferred class of these polyamine N-oxides are the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group. Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyridine, pyrrole, imidazole and derivatives thereof.

Another preferred class of polyamine N-oxides are the polyamine oxides having the general formula (I) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is attached to said R groups. Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof.

The amine N-oxide polymers of the present invention typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However the amount of amine oxide groups present in the polyamine N-oxide containing polymer can be varied by appropriate copolymerization or by appropriate degree of N-oxidation. Preferably, the ratio of amine to amine N-oxide is from 2:3 to 1:1,000,000. More preferably from 1:4 to 1:1,000,000, most preferably from 1:7 to 1:1,000,000. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is either an amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a pKa < 10, preferably pKa < 7, more preferred pKa < 6.

The polyamine N-oxide containing polymers can be obtained in almost any degree of polymerisation. The degree

of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power. Typically, the average molecular weight of the polyamine N-oxide containing polymers is within the range of 500 to 1000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

The polyamine N-oxide containing polymers of the present invention are typically present from 0.001% to 10%, more preferably from 0.01% to 2%, most preferred from 0.05% to 1% by weight of the dye transfer inhibiting composition. The present compositions are conveniently used as additives to conventional detergent compositions for use in laundry operations. The present invention also encompasses dye transfer inhibiting compositions which will contain detergent ingredients and thus serve as detergent compositions.

Methods for making polyamine N-oxides :

The production of the polyamine N-oxide containing polymers may be accomplished by polymerizing the amine monomer and oxidizing the resultant polymer with a suitable oxidizing agent, or the amine oxide monomer may itself be polymerized to obtain the polyamine N-oxide.

The synthesis of polyamine N-oxide containing polymers can be exemplified by the synthesis of polyvinyl-pyridine N-oxide. Poly-4-vinylpyridine ex Polysciences (mw. 50,000, 5.0 g., 0.0475 mole) was predissolved in 50 ml acetic acid and treated with a peracetic acid solution (25 g of glacial acetic acid, 6.4 g of a 30% vol. solution of H_2O_2, and a few drops of H_2SO_4 give 0.0523 mols of peracetic acid) via a pipette. The mixture was stirred over 30 minutes at ambient temperature (32 °C). The mixture was then heated to 80-85 °C using an oil bath for 3 hours before allowing to stand overnight. The polymer solution then obtained is mixed with 1l of acetone under agitation. The resulting yellow brown viscous syrup formed on the bottom is washed again with 1l of aceton to yield a pale crystalline solid.
The solid was filtered off by gravity, washed with acetone and then dried over P_2O_5.
The amine : amine N-oxide ratio of this polymer is 1:4 (determined by NMR).

SURFACTANT SYSTEM :

The compositions according to the present invention comprise in addition to the polyamine-N-oxide containing polymers a surfactant system wherein the surfactant can be selected from nonionic and/or anionic and/or cationic and/or ampholytic and/or zwitterionic and/or semi-polar surfactants.

Preferred surfactant systems to be used according to the present invention comprise as a surfactant one or more of the nonionic surfactants described herein. These nonionic surfactants have found to be very useful in that the dye transfer inhibiting performance of the polyamine N-oxide containing polymers has been increased in the presence of said surfactants.

NONIONICS :

Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from 6 to 14 carbon atoms, preferably from 8 to 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from 5 to 25 moles, more preferably from 3 to 15 moles, of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include Igepal™ CO-630, marketed by the GAF Corporation; and Triton™ X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

The condensation products of primary and secondary aliphatic alcohols with from 1 to 25 moles of ethylene oxide are suitable for use as the nonionic surfactant of the nonionic surfactant systems of the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 8 to 22 carbon atoms. Preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms, more preferably from 10 to 18 carbon atoms, with from 2 to 10 moles of ethylene oxide per mole of alcohol. Examples of commercially available nonionic surfactants of this type include Tergitol™ 15-S-9 (the condensation product of C_{11}-C_{15} linear alcohol with 9 moles ethylene oxide), Tergitol™ 24-L-6 NMW (the condensation product of C_{12}-C_{14} primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; NeodolTM 45-9 (the condensation product of C_{14}-C_{15} linear alcohol with 9 moles of ethylene oxide), Neodol™ 23-6.5 (the condensation product of C_{12}-C_{13} linear alcohol with 6.5 moles of ethylene oxide), Neodol™ 45-7 (the condensation product of C_{14}-C_{15} linear alcohol with 7 moles of ethylene oxide), Neodol™ 45-4 (the condensation product of C_{14}-C_{15} linear alcohol with 4 moles of ethylene oxide) marketed by Shell Chemical Company, and KyroTM EOB (the condensation product of C_{13}-C_{15} alcohol with 9 moles ethylene oxide), marketed by The Procter

& Gamble Company.

Also useful as the nonionic surfactant of the surfactant systems of the present invention are the alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from 6 to 30 carbon atoms, preferably from 10 to 16 carbon atoms and a polysaccharide, e.g. a polyglycoside, hydrophilic group containing from 1.3 to 10, preferably from 1.3 to 3, most preferably from 1.3 to 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties (optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside). The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

Optionally, and less desirably, there can be a polyalkyleneoxide chain joining the hydrophobic moiety and the polysaccharide moiety. The preferred alkyleneoxide is ethylene oxide. Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from 8 to 18, preferably from 10 to 16, carbon atoms. Preferably, the alkyl group is a straight chain saturated alkyl group. The alkyl group can contain up to 3 hydroxy groups and/or the polyalkyleneoxide chain can contain up to 10, preferably less than 5, alkyleneoxide moieties. Suitable alkyl polysaccharides are octyl, nonyldecyl, undecyldodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexaglucosides, galactosides, lactosides, glucoses, fructosides, fructoses and/or galactoses. Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentaglucosides and tallow alkyl tetra-, penta-, and hexaglucosides.

The preferred alkylpolyglycosides have the formula

$$R^2O(C_nH_{2n}O)_t(\text{glycosyl})_x$$

wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18, preferably from 12 to 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to 10, preferably 0; and x is from 1.3 to 10, preferably from 1.3 to 3, most preferably from 1.3 to 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position 6-position, and the preceding glycosyl units 2-, 3-, 4- and/or preferably predominately the 2-position.

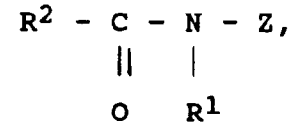
Although not preferred, the condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant of the nonionic surfactant systems of the present invention. The hydrophobic portion of these compounds will preferably have a molecular weight of from 1500 to 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available Pluronic™ surfactants, marketed by BASF.

Also suitable for use as the nonionic surfactant of the nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from 2500 to 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from 40% to 80% by weight of polyoxyethylene and has a molecular weight of from 5,000 to 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic™ compounds, marketed by BASF.

Preferred for use as the nonionic surfactant of the surfactant systems of the present invention are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from 1 to 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. Most preferred are C_8-C_{14} alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and C_8-C_{18} alcohol ethoxylates (preferably C_{10} avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

Highly preferred nonionic surfactants are polyhydroxy fatty acid amide surfactants.

Also suitable as nonionic surfactants are polyhydroxy fatty acid amide surfactants of the formula



wherein R^1 is H, or R^1 is C_{1-4} hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R^2 is C_{5-31} hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R^1 is methyl, R^2 is a straight C_{11-15} alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

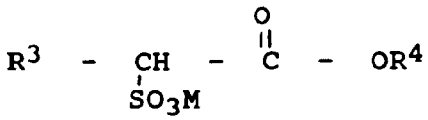
When included in such laundry detergent compositions, the nonionic surfactant systems of the present invention act to improve the greasy/oily stain removal properties of such laundry detergent compositions across a broad range of laundry conditions.

ANIONIC SURFACTANTS

Suitable anionic surfactants include alkyl alkoxylated sulfate surfactants hereof are water soluble salts or acids of the formula $RO(A)_mSO3M$ wherein R is an unsubstituted C_{10}-C_{24} alkyl or hydroxyalkyl group having a C_{10}-C_{24} alkyl component, preferably a C_{12}-C_{20} alkyl or hydroxyalkyl, more preferably C_{12}-C_{18} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between 0.5 and 6, more preferably between 0.5 and 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium or magnesium), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperidinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine or mixtures thereof. Exemplary surfactants are C_{12}-C_{18} alkyl polyethoxylate (1.0) sulfate (C_{12}-$C_{18}E(1.0)M$), C_{12}-C_{18} alkyl polyethoxylate (2.25) sulfate (C_{12}-$C_{18}E(2.25)M$), C_{12}-C_{18} alkyl polyethoxylate (3.0) sulfate (C_{12}-$C_{18}E(3.0)M$), and C_{12}-C_{18} alkyl polyethoxylate (4.0) sulfate (C_{12}-$C_{18}E(4.0)M$), wherein M is conveniently selected from sodium and potassium.

Suitable anionic surfactants to be used are alkyl ester sulfonate surfactants including linear esters of C_8-C_{20} carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO_3 according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow or palm oil.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula :



wherein R^3 is a C_8-C_{20} hydrocarbyl, preferably an alkyl, or combination thereof, R^4 is a C_1-C_6 hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R^3 is C_{10}-C_{16} alkyl, and R^4 is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R^3 is C_{10}-C_{16} alkyl.

Other suitable anionic surfactants include the alkyl sulfate surfactants hereof are water soluble salts or acids of the formula $ROSO_3M$ wherein R preferably is a C_{10}-C_{24} hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C_{10}-C_{20} alkyl component, more preferably a C_{12}-C_{18} alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperidinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof). Typically, alkyl chains of C_{12}-C_{16} are preferred for lower wash temperatures (e.g. below about 50°C) and C_{16-18} alkyl chains are preferred for higher wash temperatures (e.g. above about 50°C).

Other anionic surfactants useful for detersive purposes can also be included in the laundry detergent compositions

of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C_9-C_{20} linear alkylbenzenesulfonates, C_8-C_{22} primary of secondary alkanesulfonates, C_8-C_{24} olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C_8-C_{24} alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C_{12}-C_{18} monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C_6-C_{12} diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, and alkyl polyethoxy carboxylates such as those of the formula $RO(CH_2CH_2O)_k$-CH_2COO-M+ wherein R is a C_8-C_{22} alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23.

When included therein, the laundry detergent compositions of the present invention typically comprise from 1% to 40%, preferably from 3% to 20% by weight of such anionic surfactants.

The laundry detergent compositions of the present invention may also contain cationic, ampholytic, zwitterionic, and semi-polar surfactants, as well as nonionic surfactants other than those already described herein.

Preferred cationic surfactant systems include nonionic and ampholytic surfactants. Cationic detersive surfactants suitable for use in the laundry detergent compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyldimethylammonium halogenides, and those surfactants having the formula :

$$[R^2(OR^3)_y][R^4(OR^3)_y]_2R^5N+X-$$

wherein R^2 is an alkyl or alkyl benzyl group having from 8 to 18 carbon atoms in the alkyl chain, each R^3 is selected from the group consisting of $-CH_2CH_2-$, $-CH_2CH(CH_3)-$, $-CH_2CH(CH_2OH)-$, $-CH_2CH_2CH_2-$, and mixtures thereof; each R^4 is selected from the group consisting of C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, benzyl ring structures formed by joining the two R^4 groups, $-CH_2CHOH-CHOHCOR^6CHOHCH_2OH$ wherein R^6 is any hexose or hexose polymer having a molecular weight less than 1000, and hydrogen when y is not 0; R^5 is the same as R^4 or is an alkyl chain wherein the total number of carbon atoms of R^2 plus R^5 is not more than 18; each y is from 0 to 10 and the sum of the y values is from 0 to 15; and X is any compatible anion.

Preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula :

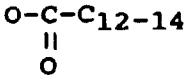
$$R_1R_2R_3R_4N^+X^- \qquad (i)$$

wherein R_1 is C_8-C_{16} alkyl, each of R_2, R_3 and R_4 is independently C_1-C_4 alkyl, C_1-C_4 hydroxy alkyl, benzyl, and $-(C_2H_4O)_xH$ where x has a value from 2 to 5, and X is an anion. Not more than one of R_2, R_3 or R_4 should be benzyl. The preferred alkyl chain length for R_1 is C_{12}-C_{15} particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R_2R_3 and R_4 are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulphate, acetate and phosphate ions.

Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are :

coconut trimethyl ammonium chloride or bromide;
coconut methyl dihydroxyethyl ammonium chloride or bromide;
decyl triethyl ammonium chloride;
decyl dimethyl hydroxyethyl ammonium chloride or bromide;
C_{12-15} dimethyl hydroxyethyl ammonium chloride or bromide;
coconut dimethyl hydroxyethyl ammonium chloride or bromide;
myristyl trimethyl ammonium methyl sulphate;
lauryl dimethyl benzyl ammonium chloride or bromide;
lauryl dimethyl $(ethenoxy)_4$ ammonium chloride or bromide;

choline esters (compounds of formula (i) wherein R_1 is $-CH_2-$



alkyl and R_2, R_3 and R_4 are methyl).

di-alkyl imidazolines [compounds of formula (i)].

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980.

When included therein, the laundry detergent compositions of the present invention typically comprise from 0% to 25%, preferably from 3% to 15% by weight of such cationic surfactants.

Ampholytic surfactants are also suitable for use in the laundry detergent compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight- or branched-chain. One of the aliphatic substituents contains at least 8 carbon atoms, typically from 8 to 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35, for examples of ampholytic surfactants.

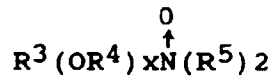
When included therein, the laundry detergent compositions of the present invention typically comprise from 0% to 15%, preferably from 1% to 10% by weight of such ampholytic surfactants.

Zwitterionic surfactants are also suitable for use in laundry detergent compositions. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38 through column 22, line 48, for examples of zwitterionic surfactants.

When included therein, the laundry detergent compositions of the present invention typically comprise from 0% to 15%, preferably from 1% to 10% by weight of such zwitterionic surfactants.

Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from 10 to 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from 10 to 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from 10 to 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from 1 to 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula



wherein R^3 is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures therof containing from 8 to 22 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms or mixtures thereof; x is from 0 to 3; and each R^5 is an alkyl or hydroxyalkyl group containing from 1 to 3 carbon atoms or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. The R^5 groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C_{10}-C_{18} alkyl dimethyl amine oxides and C_8-C_{12} alkoxy ethyl dihydroxy ethyl amine oxides.

When included therein, the laundry detergent compositions of the present invention typically comprise from 0% to 15%, preferably from 1% to 10% by weight of such semi-polar nonionic surfactants.

The present invention further provides laundry detergent compositions comprising at least 1% by weight, preferably from 3% to 65%, more preferably from 10% to 25% by weight of total surfactants.

DETERGENT ADJUNCTS

The compositions according to the present invention may further comprise a builder system. Any conventional

builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates and fatty acids, materials such as ethylenediamine tetraacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylenephosphonic acid. Though less preferred for obvious environmental reasons, phosphate builders can also be used herein.

Suitable builders can be an inorganic ion exchange material, commonly an inorganic hydrated aluminosilicate material, more particularly a hydrated synthetic zeolite such as hydrated zeolite A, X, B or HS.

Another suitable inorganic builder material is layered silicate, e.g. SKS-6 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate ($Na_2Si_2O_5$).

Suitable polycarboxylates containing one carboxy group include lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,082,179, while polycarboxylates containing phosphone substituents are disclosed in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran -cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane -hexacarboxylates and and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phtalic acid derivatives disclosed in British Patent No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

Preferred builder systems for use in the present compositions include a mixture of a water-insoluble aluminosilicate builder such as zeolite A or of a layered silicate (SKS-6), and a water-soluble carboxylate chelating agent such as citric acid.

A suitable chelant for inclusion in the detergent compositions in accordance with the invention is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds are the free acid form and the sodium or magnesium salt thereof. Examples of such preferred sodium salts of EDDS include Na_2EDDS and Na_4EDDS. Examples of such preferred magnesium salts of EDDS include MgEDDS and Mg_2EDDS. The magnesium salts are the most preferred for inclusion in compositions in accordance with the invention.

Especially for the liquid execution herein, suitable fatty acid builders for use herein are saturated or unsaturated C10-18 fatty acids, as well as well as the corresponding soaps. Preferred saturated species have from 12 to 16 carbon atoms in the alkyl chain. The preferred unsaturated fatty acid is oleic acid.

Preferred builder systems for use in granular compositions include a mixture of a water-insoluble aluminosilicate builder such as zeolite A, and a water-soluble carboxylate chelating agent such as citric acid.

Other builder materials that can form part of the builder system for use in granular compositions the purposes of the invention include inorganic materials such as alkali metal carbonates, bicarbonates, silicates, and organic materials such as the organic phosphonates, amiono polyalkylene phosphonates and amino polycarboxylates.

Other suitable water-soluble organic salts are the homo- or copolymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms.

Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000.

Detergency builder salts are normally included in amounts of from 10% to 80% by weight of the composition preferably from 20% to 70% and most usually from 30% to 60% by weight.

Detergent ingredients that can be included in the detergent compositions of the present invention include bleaching agents. These bleaching agent components can include one or more oxygen bleaching agents and, depending upon the bleaching agent chosen, one or more bleach activators. When present bleaching compounds will typically be present at levels of from 1% to 10%, of the detergent composition. In general, bleaching compounds are optional components in non-liquid formulations, e.g. granular detergents. If present, the amount of bleach activators will typically

be from 0.1% to 60%, more typically from 0.5% to 40% of the bleaching composition.

The bleaching agent component for use herein can be any of the bleaching agents useful for detergent compositions including oxygen bleaches as well as others known in the art. In a method aspect, this invention further provides a method for cleaning fabrics, fibers, textiles, at temperatures below 50°C, especially below 40°C, with a detergent composition containing polyamine N-oxide containing polymers, optional auxiliary detersive surfactants, optional detersive adjunct ingredients, and a bleaching agent.

The bleaching agent suitable for the present invention can be an activated or non-activated bleaching agent.

One category of oxygen bleaching agent that can be used encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of meta-chloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, U.S. Patent Application 740,446, European Patent Application 0,133,354 and U.S. Patent 4,412,934. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxycaproic acid as described in U.S. Patent 4,634,551.

Another category of bleaching agents that can be used encompasses the halogen bleaching agents. Examples of hypohalite bleaching agents, for example, include trichloro isocyanuric acid and the sodium and potassium dichloroisocyanurates and N-chloro and N-bromo alkane sulphonamides. Such materials are normally added at 0.5-10% by weight of the finished product, preferably 1-5% by weight.

Preferably, the bleaches suitable for the present invention include peroxygen bleaches. Examples of suitable water-soluble solid peroxygen bleaches include hydrogen peroxide releasing agents such as hydrogen peroxide, perborates, e.g. perborate monohydrate, perborate tetrahydrate, persulfates, percarbonates, peroxydisulfates, perphosphates and peroxyhydrates. Preferred bleaches are percarbonates and perborates.

The hydrogen peroxide releasing agents can be used in combination with bleach activators such as tetraacetylethylenediamine (TAED), nonanoyloxybenzenesulfonate (NOBS, described in US-A-4,412,934), 3,5,-trimethylhexanoloxybenzenesulfonate (ISONOBS, described in EP-A-120,591) or pentaacetylglucose (PAG), which are perhydrolyzed to form a peracid as the active bleaching species, leading to improved bleaching effect. Also suitable activators are acylated citrate esters.

The hydrogen peroxide may also be present by adding an enzymatic system (i.e. an enzyme and a substrate therefore) which is capable of generating hydrogen peroxide at the beginning or during the washing and/or rinsing process. Such enzymatic systems are disclosed in EP Patent Application 0537381 filed October 9, 1991.

Other peroxygen bleaches suitable for the present invention include organic peroxyacids such as percarboxylic acids.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. These materials can be deposited upon the substrate during the washing process. Upon irradiation with light, in the presence of oxygen, such as by hanging clothes out to dry in the daylight, the sulfonated zinc phthalocyanine is activated and, consequently, the substrate is bleached. Preferred zinc phthalocyanine and a photoactivated bleaching process are described in U.S. Patent 4,033,718. Typically, detergent compositions will contain 0.025% to 1.25%, by weight, of sulfonated zinc phthalocyanine.

Other detergent ingredients that can be included are detersive enzymes which can be included in the detergent formulations for a wide variety of purposes including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and prevention of refugee dye transfer. The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin.

Enzymes are normally incorporated at levels sufficient to provide up to 5 mg by weight, more typically 0.05 mg to 3 mg, of active enzyme per gram of the composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of B.subtilis and B. licheniforms. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames Alcalase , Savinase and Esperase by Novo Industries A/S (Denmark) and Maxatase by International Bio-Synthetics, Inc. (The Netherlands) and FN-base by Genencor, Optimase and Opticlean by MKC.

Of interest in the category of proteolytic enzymes, especially for liquid detergent compositions, are enzymes referred to herein as Protease A and Protease B. Protease A is described in European Patent Application 130,756. Protease B is described in European Patent Application No. 0251446.

Amylases include, for example, those obtained from a special strain of B.licheniforms, described in more detail in British Patent Specification No. 1,296,839 (Novo). Amylolytic proteins include, for example, Rapidase, Maxamyl (International Bio-Synthetics, Inc.) and Termamyl (Novo Industries).

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, which discloses fungal cellulase produced from Humicola insolens. Suitable cellulases are also disclosed in GB-A-

2,075,028 ; GB-A-2,095,275 and DE-A-2,247,832.

Examples of such cellulases are cellulases produced by a strain of Humicola insolens (Humicola grisea var. thermoidea), particularly the Humicola strain DSM 1800, and cellulases produced by a fungus of Bacillus N or a cellulase 212-producing fungus belonging to the genus Aeromonas, and cellulase extracted from the hepatopancreas of a marine mollusc (Dolabella Auricula Solander).

Especially suitable cellulase are the cellulase having color care benefits. Examples of such cellulases are cellulase described in European patent application No. 0495257, filed November 6, 1991 Carezyme (Novo).

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunoligical cross-reaction with the antibody of the lipase, produced by the microorganism Pseudomonas fluorescent IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P".

Especially suitable Lipase are lipase such as M1 Lipase (Ibis) and Lipolase (Novo).

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes of pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT Internation Application WO 89/099813 and in European Patent application EP No. 0540784, filed on November 6, 1991.

In liquid formulations, an enzyme stabilization system is preferably utilized. Enzyme stabilization techniques for aqueous detergent compositions are well known in the art. For example, one technique for enzyme stabilization in aqueous solutions involves the use of free calcium ions from sources such as calcium acetate, calcium formate and calcium propionate. Calcium ions can be used in combination with short chain carboxylic acid salts, preferably formates. See, for example, U.S. patent 4,318,818. It has also been proposed to use polyols like glycerol and sorbitol. Alkoxy-alcohols, dialkylglycoethers, mixtures of polyvalent alcohols with polyfunctional aliphatic amines (e.g., such as diethanolamine, triethanolamine or di-isopropanolamine), and boric acid or alkali metal borate. Enzyme stabilization techniques are additionally disclosed and exemplified in U.S. patent 4,261,868, U.S. Patent 3,600,319, and European Patent Application Publication No. 0 199 405. Non-boric acid and borate stabilizers are preferred. Enzyme stabilization systems are also described, for example, in U.S. Patents 4,261,868, 3,600,319 and 3,519,570.

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in Copending European Patent application No. 0553607 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

Especially preferred detergent ingredients are combinations with technologies which also provide a type of color care benefit. Examples of these technologies are cellulase and/or peroxidases and/or metallo catalysts for color maintance rejuvenation. Such metallo catalysts are described in copending European Patent Application No. 0596184.

In addition, it has been found that the polyamine-N-oxide containing polymers eliminate or reduce the deposition of the metallo-catalyst onto the fabrics resulting in improved whiteness benefit.

Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DT 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer. Especially preferred suds controlling agent are the suds suppressor system comprising a mixture of silicone oils and 2-alkyl-alcanols. Suitable 2-alkyl-alcanols are 2-butyl-octanol which are commercially available under the trade name Isofol 12 R.

Such suds suppressor system are described in Copending European Patent application No. 0593841 filed 10 November, 1992.

Especially preferred silicone suds controlling agents are described in Copending European Patent application N° 0573699 Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as Aerosil^{R}.

The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight.

Other components used in detergent compositions may be employed, such as soil-suspending agents soil-release agents, optical brighteners, abrasives, bactericides, tarnish inhibitors, coloring agents and/or encapsulated or more

encapsulated perfumes.

Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts. Polymers of this type include the polyacrylates and maleic anhydride-acrylic acid copolymers previously mentioned as builders, as well as copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

Preferred optical brighteners are anionic in character, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino-s-triazin-6-ylamino) stilbene-2:2'-disulphonate, disodium 4,-4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylaminostilbene-2:2'- disulphonate, disodium 4,4'-bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2'-disulphonate, monosodium 4',4"-bis-(2,4-dianilino-s-triazin-6 ylamino)stilbene-2-sulphonate, disodium 4,4'-bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2'-disulphonate, disodium 4,4'-bis-(4 phenyl-2,1,3-triazol-2-yl)-stilbene-2,2'-disulphonate, disodium 4,4'-bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2'disulphonate and sodium 2(stilbyl-4"-(naphtho-1',2':4,5)-1,2,3-triazole-2"-sulphonate.

Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

Soil release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0 272 033. A particular preferred polymer in accordance with EP-A-0 272 033 has the formula

$$(CH_3(PEG)_{43})_{0.75}(POH)_{0.25}[T\text{-}PO)_{2.8}(T\text{-}PEG)_{0.4}]T(PO\text{-}H)_{0.25}((PEG)_{43}CH_3)_{0.75}$$

where PEG is $-(OC_2H_4)O-$,PO is (OC_3H_6O) and T is $(pCOC_6H_4CO)$.

Also very useful are modified polyesters as random copolymers of dimethyl terephtalate, dimethyl sulfoisophtalate, ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulphobenzoate and secondarily of mono esters of ethylene glycol and/or propane-diol. The target is to obtain a polymer capped at both end by sulphobenzoate groups, "primarily", in the present context most of said copolymers herein will be end-capped by sulphobenzoate groups. However, some copolymers will be less than fully capped, and therefore their end groups may consist of monoester of ethylene glycol and/or propane 1-2 diol, thereof consist "secondarily" of such species.

The selected polyesters herein contain about 46% by weight of dimethyl terephtalic acid, about 16% by weight of propane -1.2 diol, about 10% by weight ethylene glycol, about 13% by weight of dimethyl sulfobenzoic acid and about 15% by weight of sulfoisophtalic acid, and have a molecular weight of about 3.000. The polyesters and their method of preparation are described in detail in EPA 311 342.

The detergent compositions according to the invention can be in liquid, paste, gels or granular forms. Granular compositions according to the present invention can also be in "compact form", i.e. they may have a relatively higher density than conventional granular detergents, i.e. from 550 to 950 g/l; in such case, the granular detergent compositions according to the present invention will contain a lower amount of "inorganic filler salt", compared to conventional granular detergents; typical filler salts are alkaline earth metal salts of sulphates and chlorides, typically sodium sulphate; "compact" detergents typically comprise not more than 10% filler salt. The liquid compositions according to the present invention can also be in "concentrated form", in such case, the liquid detergent compositions according to the present invention will contain a lower amount of water,compared to conventional liquid detergents. Typically, the water content of the concentrated liquid detergent is less than 30%, more preferably less than 20%, most preferably less than 10% by weight of the detergent compositions. Other examples of liquid compositions are anhydrous compositions containing substantially no water. Both aqueous and non-aqueous liquid compositions can be structured or non-structured.

The present invention also relates to a process for inhibiting dye transfer from one fabric to another of solubilized and suspended dyes encountered during fabric laundering operations involving colored fabrics.

The process comprises contacting fabrics with a laundering solution as hereinbefore described.

The process of the invention is conveniently carried out in the course of the washing process. The washing process is preferably carried out at 5 °C to 75 °C, especially 20 to 60, but the polymers are effective at up to 95°C and higher temperatures. The pH of the treatment solution is preferably from 7 to 11, especially from 7.5 to 10.5.

The process and compositions of the invention can also be used as detergent additive products.
Such additive products are intended to supplement or boost the performance of conventional detergent compositions.

The detergent compositions according to the present invention include compositions which are to be used for cleaning substrates, such as fabrics, fibers or hard surfaces, for example hard surface cleaning compositions (with or without abrasives), laundry detergent compositions, automatic and non automatic dishwashing compositions.

The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention, said scope being determined according to claims which follow.

A liquid detergent composition according to the present invention is prepared, having the following compositions:

Table I

% by weight of the total detergent composition	
Fatty acid	10
Oleic acid	4
Citric acid	1
NaOH	3.4
Propanediol	1.5
Ethanol	10

EXAMPLE I :

The extent of dye transfer from different colored fabrics was studied using a launder-o-meter test that simulates a 30 min wash cycle. The launder-o-meter beaker contains 200 ml of a detergent solution, a 10cmx10cm piece of the colored fabric and a multifiber swatch which is used as a pick-up tracer for the bleeding dye. The multifiber swatch consists of 6 pieces (1.5cmx5cm each) of different material (polyacetate, cotton, polyamide, polyester, wool and orlon) which are sewn together.

The extent of dye transfer is assessed by a Hunter Colour measurement. The Hunter Colour system evaluates the colour of a fabric sample in terms of the ΔE value which represents the change in the Hunter L, a, b, values which are determined by reflecting spectrometrie. The ΔE value is defined by the following equation:

$$\Delta E = \{(a_f - a_i)^2 + (b_f - b_i)^2 + (L_f - L_i)^2\}^{1/2}$$

where the subscripts i and f refer to the Hunter value before and after washing in the presence of the bleeding fabric, respectively. The least significant difference is 1 at 95% confidence level.

Example I demonstrates the enhanced dye transfer inhibiting performance of the nonionic surfactants in combination with the polyamine N-oxide containing polymers.

The surfactant that is used is a nonionic surfactant manufactured by Shell and sold under the Tradename Dobanol.

The dye transfer inhibiting performance was determined by measuring the whiteness of textile items washed with compositions containing the nonionic and/or the polyamine N-oxide containing polymers.

Experimental conditions:

pH =7.8

Washing temperature 40°C

A. A detergent composition according to Table I which contains no nonionic and no PVNO (poly(4-vinylpyridine-N-oxide).

B: A detergent composition according to Table I which contains nonionic (Dobanol 45/11) (270 ppm) and no PVNO (poly(4-vinylpyridine-N-oxide)).

C: A detergent composition according to Table I containing 6 ppm of PVNO (poly(4-vinylpyridine-N-oxide)) which has an average molecular weight of 10,000 and an amine to amine N-oxide ratio of 1: 10 (determined by NMR).

D : A detergent composition according to Table I containing 6 ppm of PVNO (poly(4-vinylpyridine-N-oxide)) which has an average molecular weight of about 10,000 and an amine to amine N-oxide ratio of 1:10 and 270 ppm nonionic (Dobanol 45/11).

Results: ΔE values for the cotton pick-up tracer.					
Bleeding fabric composition	Bleeding fabric color	A	B	C	D
100% cotton	Direct blue 90	13.1	12	9.4	5.1

EXAMPLE II (A/B/C)

A liquid detergent composition according to the present invention is prepared, having the following compositions :

% by weight of the total detergent composition			
	A	B	C
Linear alkylbenzene sulfonate	10	-	-
Alkyl alkoxylated sulfate	-	9	-
Polyhydroxy fatty acid	-	-	9
Trimethyl ammonium chloride C12-C14	-	-	4
Alkyl sulphate	4	4	4
Fatty alcohol (C_{12}-C_{15}) ethoxylate	12	12	12
Fatty acid	10	10	10
Oleic acid	4	4	4
Citric acid	1	1	1
Diethylenetriaminepentamethylene Phosphonic acid	1.5	1.5	1.5
NaOH	3.4	3.4	3.4
Propanediol	1.5	1.5	1.5
Ethanol	10	10	10
Ethoxylated tetraethylene pentamine	0.7	0.7	0.7
Poly(4-vinylpyridine)-N-oxide	0-1	0-1	0-1
Thermamyl	0.13	0.13	0.13
Carezyme	0.014	0.014	0.014
FN-Base	1.8	1.8	1.8
Lipolase	0.14	0.14	0.14
Endoglucanase A	0.53	0.53	0.53
Suds supressor (ISOFOLr)	2.5	2.5	2.5
Minors	up to 100		

EXAMPLE III (A/B/C)

A compact granular detergent composition according to the present invention is prepared, having the following formulation:

% by weight of the total detergent composition			
	A	B	C
Linear alkyl benzene sulphonate	11.40	-	-
Alkyl alkoxylated sulfate	-	10	-
Polyhydroxy fatty acid	-	-	9
Trimethyl ammonium chloride C12-C14	-	-	4
Tallow alkyl sulphate	1.80	1.80	1.80
C_{45} alkyl sulphate	3.00	3.00	3.00
C_{45} alcohol 7 times ethoxylated	4.00	4.00	4.00
Tallow alcohol 11 times ethoxylated	1.80	1.80	1.80
Dispersant	0.07	0.07	0.07

(continued)

% by weight of the total detergent composition			
	A	B	C
Silicone fluid	0.80	0.80	0.80
Trisodium citrate	14.00	14.00	14.00
Citric acid	3.00	3.00	3.00
Zeolite	32.50	32.50	32.50
Maleic acid actylic acid copolymer	5.00	5.00	5.00
Cellulase (active protein)	0.03	0.03	0.03
Alkalase/BAN	0.60	0.60	0.60
Lipase	0.36	0.36	0.36
Sodium silicate	2.00	2.00	2.00
Sodium sulphate	3.50	3.50	3.50
Poly(4-vinylpyridine)-N-oxide	0-1	0-1	0-1
Minors	up to 100		

The above compositions (Example I(A/B/C) and II(A/B/C)) were very good at displaying excellent clay and detergent performance with outstanding color-care performance on colored fabrics and mixed loads of colored and white fabrics.

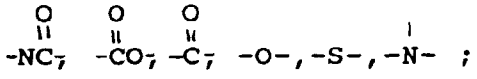
Claims

1. A dye transfer inhibiting composition comprising a polymer selected from

a) polyamine N-oxide containing polymers which contain units having the following structure formula :

wherein

P is a polymerisable unit, whereto the N-O group can be attached to or wherein the N-O group forms part of the polymerisable unit.
A is



x is or 0 or 1;
R are aliphatic, aromatic, heterocyclic or alicyclic groups whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups with the proviso that R is not an ethoxylated group,

b) a surfactant system comprising a surfactant selected from nonionic and/or anionic and/or cationic and/or

ampholytic and/or zwitterionic and/or semi-polar surfactants.

2. A dye transfer inhibiting composition according to claim 1 wherein P is a polymerisable unit wherein the N-O group is attached to and wherein R is selected from an aromatic or heterocyclic group.

3. A dye transfer inhibiting composition according to claim 2 wherein the nitrogen of the N-O group forms part of the R-group.

4. A dye transfer inhibiting composition according to claim 3 wherein the R-group is selected from pyridine, pyrrole, imidazole and derivatives thereof.

5. A dye transfer inhibiting composition according to claim 1,2 wherein the nitrogen of the N-O group is attached to the R-group.

6. A dye transfer inhibiting composition according to claim 5 wherein R is a phenyl group.

7. A dye transfer composition according to claim 1 wherein P is a polymerisable unit, whereto the N-O group forms part of the polymerisable unit and wherein R is selected from an aromatic or heterocyclic group.

8. A dye transfer inhibiting composition according to claim 7 wherein the nitrogen of the N-0 group forms part of the R-group.

9. A dye transfer inhibiting composition according to claim 8 wherein the R-group is selected from pyridine, pyrrole, imidazole and derivatives thereof.

10. A dye transfer inhibiting composition according to claim 1-9 wherein the polymeric backbone is derived from the group of the polyvinyl polymers.

11. A dye transfer inhibiting composition according to claims 1-10 wherein the ratio of amine to amine N-oxide is from 2:3 to 1:1,000,000, preferably from 1:4 to 1:1,000,000, most preferably from 1:7 to 1:1,000,000.

12. A dye transfer inhibiting composition according to claims 1-11 wherein the polyamine N-oxide containing polymer has an average molecular weight within the range of 500 to 1,000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

13. A dye transfer inhibiting composition according to claims 1-12 wherein said polyamine N-oxide containing polymer is poly(4-vinylpyridine-N-oxide).

14. A dye transfer inhibiting composition according to claims 1-13 wherein the polyamine N-oxide is present at levels from 0.001% to 10 % by weight of the composition.

15. A dye transfer inhibiting composition according to claims 1-14 wherein said surfactant system comprises a nonionic surfactant.

16. A dye transfer inhibiting composition according to claim 15 further comprising a surfactant selected from an anionic surfactant or a cationic and/or amphoteric surfactant.

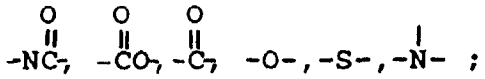
17. A dye transfer inhibiting composition which is a detergent additive, in the form of a non-dusting granule or a liquid.

18. A detergent composition which comprises a dye transfer inhibiting composition according to claims 1-17 further comprising other conventional detergent ingredients.

19. Use of a polymer selected from polyamine N-oxide containing polymers which contain units having the following structure formula:

wherein

P is a polymerisable unit, whereto the N-O group can be attached to or wherein the N-O group forms part of the polymerisable unit.
A is



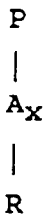
x is 0 or 1;
R are aliphatic, ethoxylated aliphatic, aromatic, heterocyclic or alicyclic groups whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups and

a surfactant system comprising a surfactant selected from nonionic and/or anionic and/or cationic and/or ampholytic and/or zwitterionic and/or semi-polar surfactants, for inhibiting dye transfer between fabrics during washing.

Patentansprüche

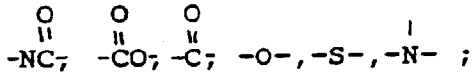
1. Die Farbstoffübertragung inhibierende Zusammensetzung, umfassend ein Polymer, gewählt aus

a) Polyamin-N-oxid enthaltenden Polymeren, welche Einheiten der folgenden Strukturformel enthalten:



worin

bedeuten: P eine polymerisierbare Einheit, an welche die N-O-Gruppe gebunden werden kann, oder worin die N-O-Gruppe ein Teil der polymerisierbaren Einheit bildet;
A



x 0 oder 1;
R aliphatische, aromatische, heterocyclische oder alicyclische Gruppen, an welche der Stickstoff der N-

O-Gruppe gebunden sein kann, oder worin der Stickstoff der N-O-Gruppe ein Teil dieser Gruppen ist, mit der Maßgabe, daß R keine ethoxylierte Gruppe ist,

b) ein Tensidsystem, umfassend ein Tensid, gewählt aus nichtionischen und/oder anionischen und/oder kationischen und/oder ampholytischen und/oder zwitterionischen und/oder semipolaren Tensiden.

2. Die Farbstoffübertragung inhibierende Zusammensetzung nach Anspruch 1, wobei P eine polymerisierbare Einheit ist, an welche die N-O-Gruppe gebunden ist, und wobei R aus einer aromatischen oder heterocyclischen Gruppe gewählt ist.

3. Die Farbstoffübertragung inhibierende Zusammensetzung nach Anspruch 2, wobei der Stickstoff der N-O-Gruppe einen Teil der R-Gruppe bildet.

4. Die Farbstoffübertragung inhibierende Zusammensetzung nach Anspruch 3, wobei die R-Gruppe aus Pyridin, Pyrrol, Imidazol und Derivaten hiervon gewählt ist.

5. Die Farbstoffübertragung inhibierende Zusammensetzung nach Anspruch 1 oder 2, wobei der Stickstoff der N-O-Gruppe an die R-Gruppe gebunden ist.

6. Die Farbstoffübertragung inhibierende Zusammensetzung nach Anspruch 5, wobei R eine Phenylgruppe ist.

7. Die Farbstoffübertragung inhibierende Zusammensetzung nach Anspruch 1, wobei P eine polymerisierbare Einheit ist, wobei die N-O-Gruppe einen Teil der polymerislerbaren Einheit bildet, und wobei R aus einer aromatischen oder heterocyclischen Gruppe gewählt ist.

8. Die Farbstoffübertragung inhibierende Zusammensetzung nach Anspruch 7, wobei der Stickstoff der N-O-Gruppe einen Teil der R-Gruppe bildet.

9. Die Farbstoffübertragung inhibierende Zusammensetzung nach Anspruch 8, wobei die R-Gruppe aus Pyridin, Pyrrol, Imidazol und Derivaten hiervon gewählt ist.

10. Die Farbstoffübertragung inhibierende Zusammensetzung nach den Ansprüchen 1-9, wobei das polymere Grundgerüst aus der Gruppe der Polyvinylpo-lymeren abgeleitet ist.

11. Die Farbstoffübertragung inhibierende Zusammensetzung nach den Ansprüchen 1-10, wobei das Verhältnis von Amin zu Amin-N-oxid 2:3 bis 1:1.000.000, vorzugsweise 1:4 bis 1:1.000.000, am meisten bevorzugt 1:7 bis 1:1.000.000 beträgt.

12. Die Farbstoffübertragung inhibierende Zusammensetzung nach den Ansprüchen 1-11, wobei das Polyamin-N-oxid enthaltende Polymer ein Durchschnittsmolekulargewicht innerhalb des Bereichs von 500 bis 1.000.000; vorzugsweise 1.000 bis 50.000, weiter vorzugsweise 2.000 bis 30.000, am meisten bevorzugt 3.000 bis 20.000, aufweist.

13. Die Farbstoffübertragung inhibierende Zusammensetzung nach den Ansprüchen 1-12, wobei das Polyamin-N-oxid enthaltende Polymer Poly(4-vinylpyridin-N-oxid) ist.

14. Die Farbstoffübertragung inhibierende Zusammensetzung nach den Ansprüchen 1-13, wobei das Polyamin-N-oxid in Anteilen von 0,001 bis 10 Gew.-% der Zusammensetzung vorliegt.

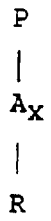
15. Die Farbstoffübertragung inhibierende Zusammensetzung nach den Ansprüchen 1-14, wobei das Tensidsystem ein nichtionisches Tensid umfaßt.

16. Die Farbstoffübertragung inhibierende Zusammensetzung nach Anspruch 15, umfassend weiterhin ein Tensid, gewählt aus einem anionischen Tensid oder einem kationischen und/oder amphoteren Tensid.

17. Die Farbstoffübertragung inhibierende Zusammensetzung, welche ein Waschmitteladditiv ist, in Form eines nichtstaubenden Granulats oder einer Flüssigkeit.

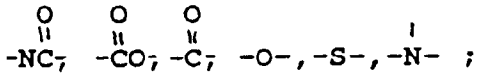
18. Waschmittelzusammensetzung, umfassend eine die Farbstoffübertragung inhibierende Zusammensetzung nach den Ansprüchen 1-17, umfassend weiterhin weitere herkömmliche Waschmittelbestandteile.

19. Verwendung eines Polymeren, gewählt aus Polyamin-N-oxid enthaltenden Polymeren, welche Einheiten der folgenden Strukturformel enthalten:



worin bedeuten:

P eine polymerisierbare Einheit, an welche die N-O-Gruppe gebunden werden kann, oder worin die N-O-Gruppe ein Teil der polymerisierbaren Einheit bildet;
A



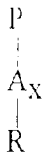
x 0 oder 1;
R aliphatische, ethoxylierte aliphatische, aromatische, heterocyclische oder alicyclische Gruppen, an welche der Stickstoff der N-O-Gruppe gebunden sein kann, oder worin der Stickstoff der N-O-Gruppe ein Teil dieser Gruppen ist, und

eines Tensidsystems, umfassend ein Tensid, gewählt aus nichtionischen und/oder anionischen und/oder kationischen und/oder ampholytischen und/oder zwitterionischen und/oder semipolaren Tensiden, zur Inhibierung der Farbstoffübertragung zwischen Textilien während dem Waschen.

Revendications

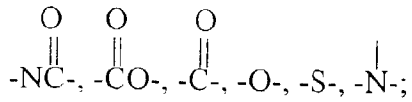
1. Composition inhibant le transfert de teintures comprenant un polymère choisi parmi

a) les polymères contenant un poly(N-oxyde d'amine) comportant des motifs de formule développée suivante:



dans laquelle

P est un motif polymérisable, auquel le groupe N-O peut être fixé ou dont fait partie le groupe N-O,
A est



x vaut 0 ou 1;
R est un groupe aliphatique, aromatique, hétérocyclique ou alicyclique auquel l'atome d'azote du groupe N-O peut être fixé ou dont fait partie l'atome d'azote du groupe N-O, à la condition que R ne soit pas un groupe éthoxylé,

b) un système tensioactif comprenant un tensioactif choisi parmi les tensioactifs non ioniques et/ou anioniques et/ou cationiques et/ou ampholytes et/ou zwittérioniques et/ou semi-polaires.

2. Composition inhibant le transfert de teintures selon la revendication 1, dans laquelle P est un motif polymérisable auquel le groupe N-O est fixé et dans laquelle R est choisi parmi un groupe aromatique et un groupe hétérocyclique.

3. Composition inhibant le transfert de teintures selon la revendication 2, dans laquelle l'atome d'azote du groupe N-O fait partie du groupe R.

4. Composition inhibant le transfert de teintures selon la revendication 3, dans laquelle le groupe R est choisi parmi la pyridine, le pyrrole, l'imidazole et leurs dérivés.

5. Composition inhibant le transfert de teintures selon la revendication 1 ou 2, dans laquelle l'atome d'azote du groupe N-O est fixé au groupe R.

6. Composition inhibant le transfert de teintures selon la revendication 5, dans laquelle le groupe R est un groupe phényle.

7. Composition inhibant le transfert de teintures selon la revendication 1, dans laquelle P est un motif polymérisable dont fait partie le groupe N-O et dans laquelle R est choisi parmi un groupe aromatique et un groupe hétérocyclique.

8. Composition inhibant le transfert de teintures selon la revendication 7, dans laquelle l'atome d'azote du groupe N-O fait partie du groupe R.

9. Composition inhibant le transfert de teintures selon la revendication 8, dans laquelle le groupe R est choisi parmi la pyridine, le pyrrole, l'imidazole et leurs dérivés.

10. Composition inhibant le transfert de teintures selon les revendications 1 à 9, dans laquelle le squelette polymère est dérivé du groupe des polymères polyvinyliques.

11. Composition inhibant le transfert de teintures selon les revendications 1 à 10, clans laquelle le rapport des groupes amine aux groupes N-oxyde d'amine est de 2:3 à 1:1 000 000, de préférence de 1:4 à 1:1 000 000, tout particulièrement de 1:7 à 1:1 000 000.

12. Composition inhibant le transfert de teintures selon les revendications 1 à 11, dans laquelle le polymère contenant un poly(N-oxyde d'amine) possède une masse moléculaire moyenne dans la gamme de 500 à 1 000 000, de préférence de 1 000 à 50 000, mieux encore de 2 000 à 30 000, tout particulièrement de 3 000 à 20 000.

13. Composition inhibant le transfert de teintures selon les revendications 1 à 12, dans laquelle ledit polymère contenant un poly(N-oxyde d'amine) est le poly(N-oxyde de 4-vinylpyridine).

14. Composition inhibant le transfert de teintures selon les revendications 1 à 13, dans laquelle le poly(N-oxyde d'amine) est présent dans une proportion de 0,001 à 10% en poids de la composition.

15. Composition inhibant le transfert de teintures selon les revendications 1 à 14. dans laquelle ledit système tensioactif comprend un tensioactif non ionique.

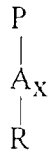
16. Composition inhibant le transfert de teintures selon la revendication 15, comprenant en outre un tensioactif choisi

parmi un tensioactif anionique ou un tensioactif cationique et/ou amphotère.

17. Composition inhibant le transfert de teintures, qui est un additif pour détergents, sous forme d'un granulé non poussiéreux ou d'un liquide.

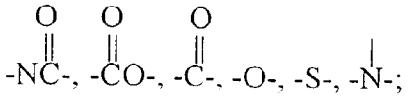
18. Composition détergente qui comprend une composition inhibant le transfert de teintures selon les revendications 1 à 17 et qui comprend en outre d'autres ingrédients détergents classiques.

19. Utilisation d'un polymère choisi parmi les polymères contenant un poly(N-oxyde d'amine) comportant des motifs de formule développée suivante:



dans laquelle

P est un motif polymérisable, auquel le groupe N-O peut être fixé ou dont fait partie le groupe N-O,
A es



x vaut 0 ou 1;
R est un groupe aliphatique, aliphatique éthoxylé, aromatique, hétérocyclique ou alicyclique auquel l'atome d'azote du groupe N-O peut être fixé ou dont fait partie l'atome d'azote du groupe N-O, et
d'un système tensioactif comprenant un tensioactif choisi parmi les tensioactifs non ioniques et/ou anioniques et/ou cationiques et/ou ampholytes et/ou zwittérioniques et/ou semi-polaires,

pour inhiber le transfert de teintures entre des tissus pendant un lavage.